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Title: Application of Laser Induced Breakdown Spectroscopy (LIBS) to Mars Polar Exploration: LIBS Analysis of Water Ice and Water Ice/Soil Mixtures

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APPLICATION OF LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) TO MARS POLAR EXPLORATION: LIBS ANALYSIS OF WATER ICE AND WATER ICE/SOIL MIXTURES. Z. A. Arp[1], D. A. Cremers[2], R.C. Wiens[3], [1]Nuclear Materials and Technology, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; zaa@lanl.gov), [2]Chemical Diagnostics and Instrumentation, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; cremers_david@lanl.gov), [3]Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545 USA; rwiens@lanl.gov).

Introduction: The polar regions of Mars are of great interest due to the presence of water ice and CO_2 ice combined with wind blown deposits. Due to seasonal changes and repeated cycles of precipitating dusts and H_2O, geological samples appear to have built up in the polar regions. These polar layered deposits (PLD) may include volcanic ash, fallout from surface impacts, evaporates from subliming lakes and seas, and even wind blown ancient microbial life[1]. The ability to examine the PLDs will be of great importance in the study of past Martian geological history and the determination of the past presence of life on Mars.

Analysis of the ice fields which are present in the polar regions of Mars will almost certainly be of great interest to future surface rovers and landers to this region. The use of LIBS will maximize the scientific return of these missions. Through the development of a compact sensor head and a pan and tilt mechanism, analysis of PLD may be made in areas that are otherwise inaccessible to either a lander or a surface rover. This gives LIBS a significant advantage over other analysis techniques which require more than just optical access. Also, through the use of repetitive laser pulses it will be possible to ablate away the water ice layer to better examine the PLDs which exist below the surface. Another potential use for LIBS is the analysis of retrieved ice core samples. Laser pulses formed along the length of the ice core can monitor composition as a function of depth. This method has already been shown to work for mineral drill cores and terrestrial ice cores using laser ablation ICP-MS[2,3].

Prior work on the use of LIBS for analysis of ice has focused on the detection of trace metal ions in the ice[4]. To our knowledge no further work has been reported on the use of LIBS for analysis of water ice and water ice/soil mixtures. Here we will examine in detail the detection capabilities of LIBS on water ice and water ice/soil mixtures in an atmosphere similar in pressure and composition to that on Mars.

Experimental: Fig. 1 shows the experimental setup used to acquire LIBS spectra of water ice and water/ice soil mixtures. In this work a Q-switched Nd:YAG laser (1064 nm) was used for ablation. Elemental emission was detected using either a Catalina Sciences SE 200 echellete spectrometer or a Chromex 250 IS spectrometer. Light was collected for these spectrometers by focusing the emitted plasma light onto a fiber optic cable using a quartz (100 mm dia.) 1 m focal length collection lens. In order to counter the effects of chromatic aberration the fiber optic was positioned in the focal region which produced the most intense spectra across the region of interest (200-800 nm).

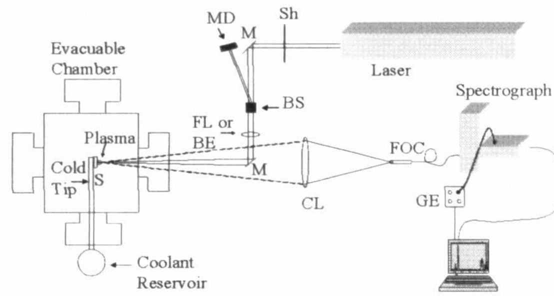

Fig. 1 Experimental setup for analysis of ice/soil mixtures. Sh=shutter; M-mirror; MD-Power meter; BS-Beam Splitter; FL-Focal Lens; BE-Beam Expander; S-Sample; CL- 100 mm diam. collection len; FOC-fiber optic cable; GE-gating electronics

Water ice/soil samples were made by quickly freezing a slurry of deionized water and the soil (Brammer Standards Company GBW 7703-7708) of interest. This produced a relatively homogeneous water ice/soil mixture.

Both liquid nitrogen and a eutectic dry ice/ethanol mixture were used to cool the cold tip. Originally the eutectic mixture was used to keep the CO_2 gas from condensing on the cold tip. The higher temperature of the cold tip with eutectic cooling (~246 K) as compared to liquid nitrogen cooling (~165 K) also allowed studies to be made of temperature effects. These temperatures also had the added advantage of duplicating the high and low temperatures which are found on Mars. Due to condensation of CO_2 at the lower temperatures of the liquid nitrogen cooled tip it was necessary to use air in some experiments.

Results: Multiple experiments using LIBS on ice and ice/soil mixtures have been done. Examples of the results obtained from these experiments are shown in Figs.1 and 2. In Fig. 1 the LIBS spectra from two water ice/soil mixtures of different concentrations are shown. For water ice the important lines observed are H (656.3, 486.1, and 434.0 nm) and O (700.1/700.2, 777.2, 777.4, 777.5, and 844.6 nm) lines. The lines found in water do not interfere with the monitoring of elements in soil. In the water ice/soil mixtures, some of the more prominent lines include, but are not limited to, Ca (393.4, 396.8, 315.9, and 317.9 nm), Al (396.2, 394.4, 308.2, and 309.3 nm), Na (589.0 and 589.6 nm), and Si (390.6 and 288.2 nm).

Figure 2(b) shows a graph of the dependence of element emission signals on the % weight soil in ice. Here the elements that are typically easy to excite show an almost linear behavior with respect to the addition of water ice. Elements which are typically more difficult to excite (Si(II) and Al(II) for example) show a large reduction in intensity with the initial addition of water ice. These factors are probably related to either a matrix-induced effect, a change in the electron density, or a large change in the plasma temperature.

The previous data shows that LIBS is adaptable for analysis of water ice/soil mixtures. Experiments were conducted to evaluate the use of LIBS to ablate through ice and ice/soil layers. Fig. 3 shows some of the results which were obtained. Shown here are the ablation depths reached in water ice and water ice/soil mixtures at the temperatures of the liquid nitrogen (~165 K) and the eutectic (~246 K) cooled cold tip. As can be seen there is a distinct difference in the ablation depths achieved. The eutectic cooled tip samples are ablated at a much faster rate (62 microns/pulse) and a deeper depth (~25 mm) than can be achieved with liquid nitrogen (8.7 microns/pulse and ~10 mm deep) cooled samples. Additional experimental data shows that the maximum depth that a useful spectrum can consistently be obtained under these different conditions is ~10 mm for the eutectic-cooled and ~5 mm for the liquid nitrogen cooled samples. The differences in these ablation rates is attributed to the size of the hole ablated in these samples and the difference in energy required to raise the ice temperature to its melting point.

Shown in Table 1 are the limits of detection for several elements at a standoff distance of 4 and 6.5 m and 10% by wt. soil in water ice samples. The standoff distance was limited by the physical size of the lab and not the intensity of the spectra obtained at the maximum distance.

Table 1. Detection limits as a function of distance.

Detection Limits (ppm)			
	Distance (m)		
Element	4	6.5	19 [5]
	Ice/10% soil mixtures		Dry soil
Ba	12	66	21
Li	6	3	20
Mn	15	101	---
Sr	.5	1.7	1.9
Ti	111	520	---

Conclusions: In this work it is shown that LIBS has the potential to be a useful analytical technique for the analysis of water ice, water ice/soil mixtures and core samples for a Mars polar mission.

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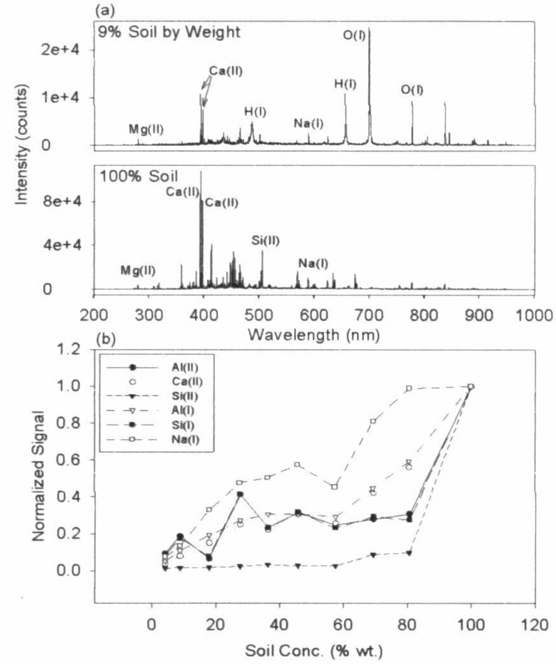

Fig. 2 (a) Spectra of water ice/soil mixtures containing 9% and 100% soil. (b) Dependence of element emissions on the %wt. soil in ice. Sample distance was 1m.

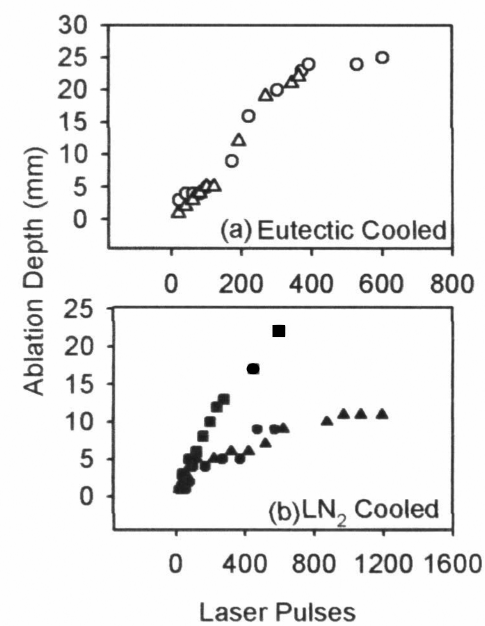

Fig. 3 Comparison of ablation depth vs. number of laser pulses using (a) a eutectic cooled cold tip [for ice (Δ) and ice/10% soil (o)] and (b) a LN_2 cooled cold tip [for ice (▲) and ice/10% soil (●)]. Ablation data for ice/10% soil is also shown in (b) using the double pulse mode of the laser (■). Sample distance was 1 m.